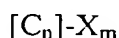


CLAIMS

1. A functionalized carbon nanotube, the surface of which carries covalently bound reactive and/or activable functional groups which are homogeneously distributed on said surface, said functionalized carbon nanotube being substantially intact and soluble in organic and/or aqueous solvents.
2. A functionalized carbon nanotube according to claim 1, wherein said carbon nanotube is a single-walled (SWNT) or a multi-walled carbon nanotube (MWNT).
3. A functionalized carbon nanotube according to claim 2, wherein the organic solvents are selected from a group comprising dimethylformamide, dichloromethane, chloroform, acetonitrile, dimethylsulfoxide, methanol, ethanol, toluene, isopropanol, 1,2-dichloroethane, N-methylpyrrolidone, tetrahydrofuran.
4. A functionalized carbon nanotube according to claim 3, of following general formula:



wherein:

C_n are surface carbons of a substantially cylindrical carbon nanotube of substantially constant diameter, said diameter being from about 0.5 to about 50 nm, in particular from about 0.5 to 5 nm for SWNTs and from about 20 to about 50 nm for MWNTs,

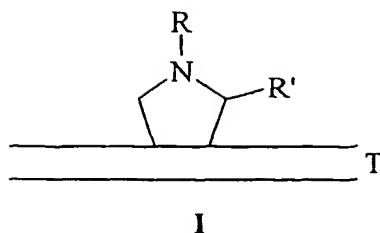
X is a functional group,

n is an integer from about $3 \cdot 10^3$ to about $3 \cdot 10^6$,

m is an integer from about $0.001n$ to about $0.1n$,

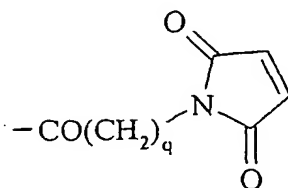
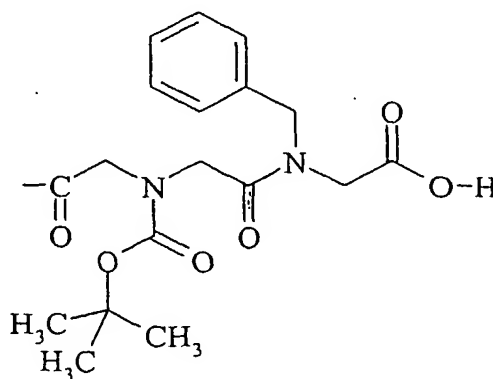
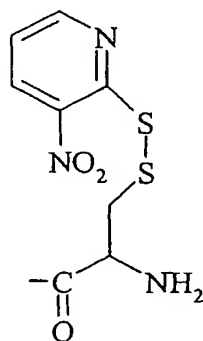
there are from about $2 \cdot 10^{-11}$ moles to about $2 \cdot 10^{-9}$ moles of X functional groups per cm^2 of carbon nanotube surface.

5. A functionalized carbon nanotube according to claim 4, wherein X is a pyrrolidine ring, of the following general formula (I):



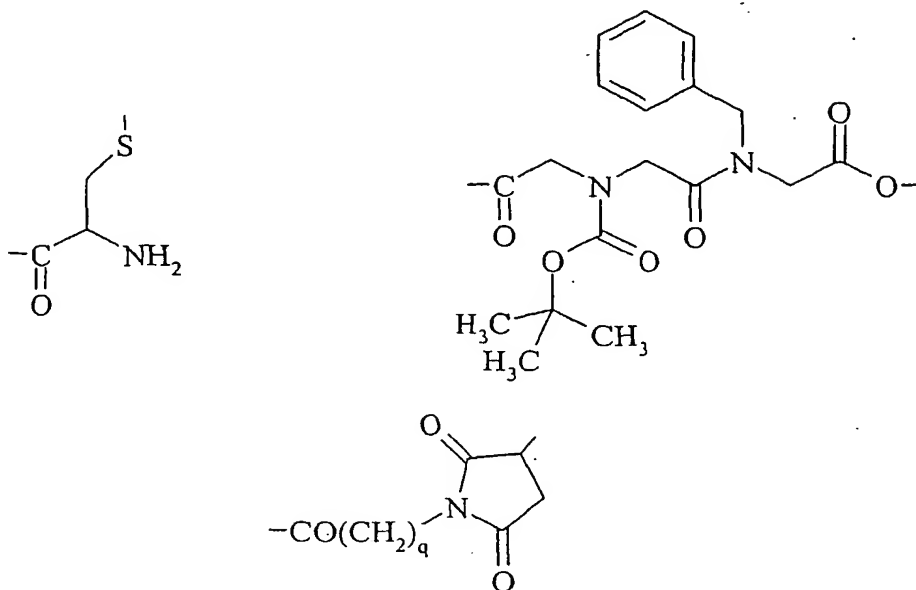
wherein T represents a carbon nanotube, and independently from each other R and R' represent -H or a group of formula -M-Y-(Z)_a-(P)_b, wherein independently from each other a and b represent 0 or 1, provided R and R' cannot simultaneously represent H, and:

- M is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising -(CH₂)_r- or -(CH₂-CH₂-O)_r-CH₂-CH₂-, wherein r is an integer from 1 to 20;
- Y is a reactive group when a=b=0, such as a group selected from the list comprising -OH, -NH₂, -COOH, -SH, -CHO, a ketone such as -COCH₃, an azide or a halide; or derived from a reactive group, when a or b is different from 0, such as a group selected from the list comprising -O-, -NH-, -COO-, -S-, -CH=, -CH₂-, -CC_kH_{2k+1}=, wherein k is an integer from 1 to 10, in particular -CCH₃=, or -CHC_kH_{2k+1}-, wherein k is an integer from 1 to 10, in particular -CHCH₃-;
- Z is a linker group, liable to be linked to a P group, and if need be to release said P group, such as a group of one of the following formulae when a=1 and b=0:



wherein q is an integer from 1 to 10;

or of one of the corresponding following formulae when $a=1$ and $b=1$:

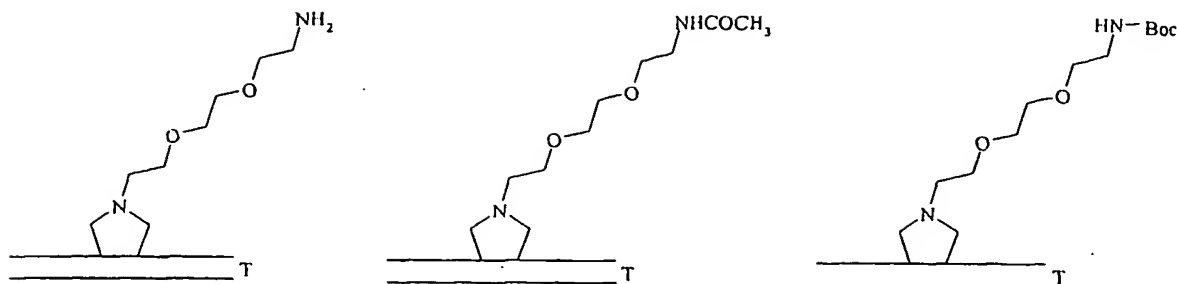


wherein q is an integer from 1 to 10;

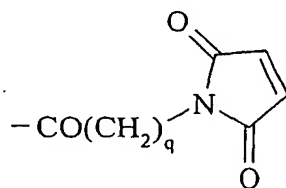
- P is an effective group allowing spectroscopic detection of said functionalized carbon nanotube, such as a fluorophore, such as FITC, or an active molecule, liable to induce a biological effect, such as an amino acid, a peptide, a pseudopeptide, a protein, such as an enzyme or an antibody, a nucleic acid, a carbohydrate, or a drug.

if appropriate at least one of Y, Z, or P groups, can be substituted by a capping group, such as $\text{CH}_3\text{CO-}$ (acetyl), methyl, or ethyl, or a protecting group such as methyl, ethyl, benzyl, *tert*-butyl, trityl, 3-nitro-2-pyridylsulfenyl, *tert*-butyloxycarbonyl (Boc), fluorenylmethyloxycarbonyl (Fmoc), benzylcarbonyl, trimethylsilylethyloxycarbonyl, phthalimide, dimethylacetal, diethylacetal or, 1,3-dioxolane.

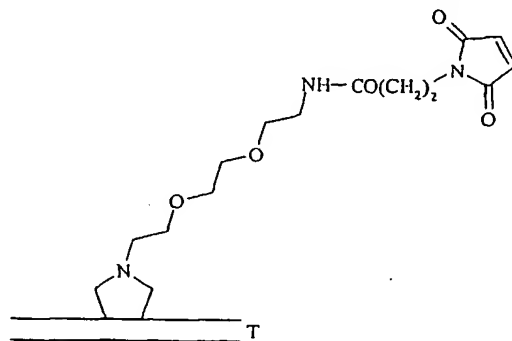
6. A functionalized carbon nanotube according to claim 5, wherein $a=b=0$ and Y is a reactive group selected from the list comprising -OH , -NH_2 , -COOH , -SH , -CHO , a ketone, such as -COCH_3 , an azide, or a halide, in particular -NH_2 , said functionalized carbon nanotube being, if appropriate, substituted by a capping or a protecting group, such as defined in claim 5, in particular a Boc or acetyl group, and being for instance a functionalized carbon nanotube of one of the following formulae:



7. A functionalized carbon nanotube according to claim 5, wherein $a=1$ and $b=0$, Y is derived from a reactive group and selected from the list comprising -O-, -NH-, -COO-, -S-, -CH=, -CH₂-, -CC_kH_{2k+1}=, wherein k is an integer from 1 to 10, in particular -CCH₃=, or -CHC_kH_{2k+1}-, wherein k is an integer from 1 to 10, in particular -CHCH₃-, and Z is as defined in claim 5 and represents in particular the group of the following formula:

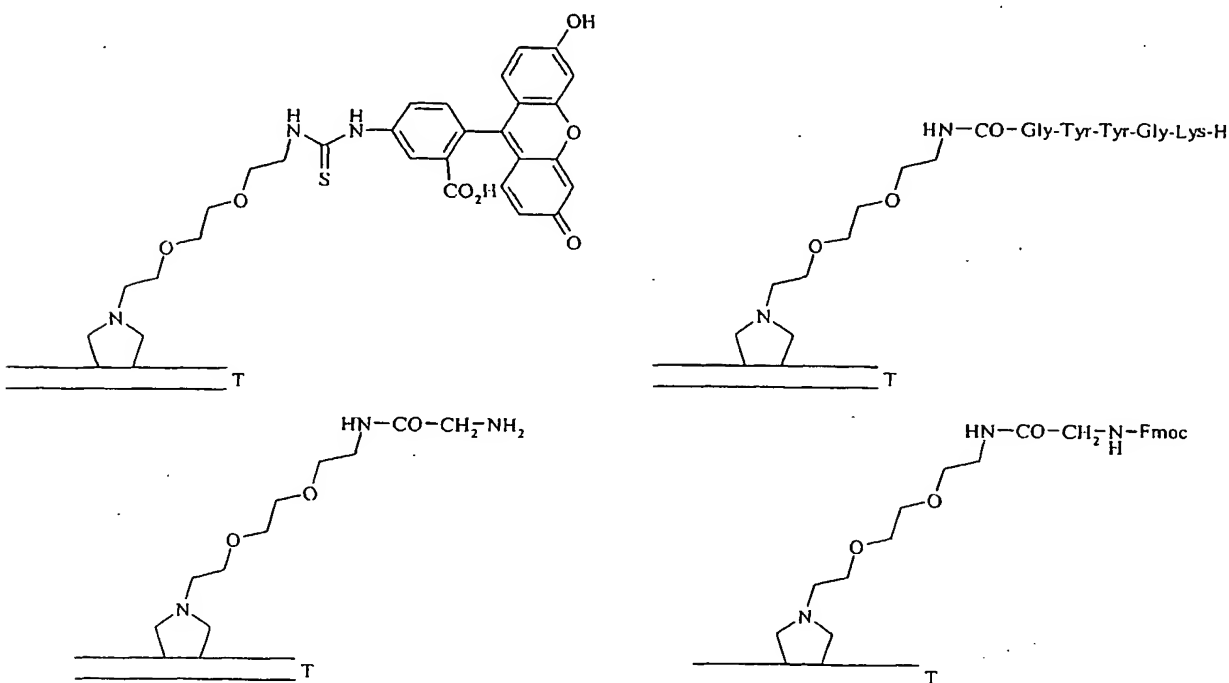


wherein q is an integer from 1 to 10, said functionalized carbon nanotube being if appropriate substituted by a protecting group, such as defined in claim 5, and being for instance the functionalized carbon nanotube of the following formula:

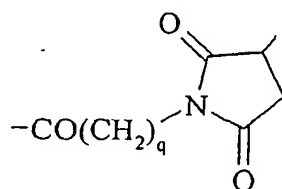


8. A functionalized carbon nanotube according to claim 5, wherein $a=0$ and $b=1$, Y is derived from a reactive group and selected from the list comprising -O-, -NH-, -COO-, -S-, -CH=, -CH₂-, -CC_kH_{2k+1}=, wherein k is an integer from 1 to 10, in particular -CCH₃=, or -CHC_kH_{2k+1}-, wherein k is an integer from 1 to 10, in particular -CHCH₃-, and P is an effective group or an active molecule, such as defined in claim 5, in particular FITC, an amino acid, such as glycine, or a peptide,

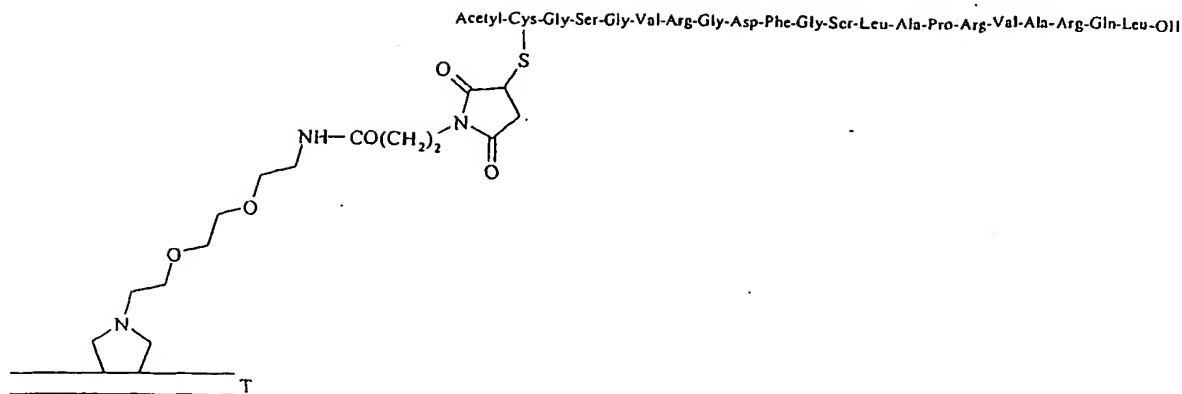
such as the peptide H-Lys-Gly-Tyr-Tyr-Gly-OH, said functionalized carbon nanotube being if appropriate substituted by a protecting group as defined in claim 5, such as Fmoc, and being for instance a functionalized carbon nanotube of one of the following formulae:



9. A functionalized carbon nanotube according to claim 5, wherein $a=1$ and $b=1$, Y is derived from a reactive group and selected from the list comprising -O-, -NH-, -COO-, -S-, -CH=, -CH₂-, -CC_kH_{2k+1}-, wherein k is an integer from 1 to 10, in particular -CCH₃-, or -CHC_kH_{2k+1}-, wherein k is an integer from 1 to 10, in particular -CHCH₃-, Z is as defined in claim 5 and represents in particular the group of the following formula:

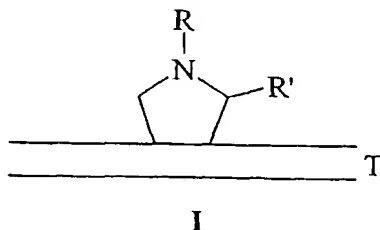


wherein q is an integer from 1 to 10, and P is as defined in claim 5, in particular a peptide, such as the peptide Acetyl-Cys-Gly-Ser-Gly-Val-Arg-Gly-Asp-Phe-Gly-Ser-Leu-Ala-Pro-Arg-Val-Ala-Arg-Gln-Leu-OH, said functionalized carbon nanotube being if appropriate substituted by a protecting group, such as defined in claim 5, and being for instance the functionalized carbon nanotube of the following formula:



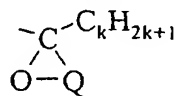
10. A functionalized carbon nanotube according to claim 8 or 9, wherein P is a peptide or a protein, said peptide or protein comprising in particular a B cell epitope or a T cell epitope, such as a T helper epitope or a T cytotoxic epitope, or a mixture thereof.

11. A process for preparing a functionalized carbon nanotube of the following formula I:

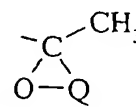


wherein T represents a carbon nanotube and independently from each other R and R' represent -H or a group of formula -M-Y, provided R and R' cannot simultaneously represent H, wherein:

- -M- is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising $-(CH_2)_r-$ or $-(CH_2-CH_2-O)_r-CH_2-CH_2-$, wherein r is an integer from 1 to 20;
- -Y is a reactive group, such as a group selected from the list comprising, -OH, -NH₂, -COOH, -SH, -CHO, a ketone such as -COCH₃, an azide, a halide, if appropriate protected, such as -O-Q, -NH-Q, -COO-Q, -S-Q, -CH(OQ)₂,



wherein k is an integer from 1 to 10, in particular



wherein Q is a protecting group or forms a protecting group with the adjacent atoms to which it is linked;

said process comprising the following step:

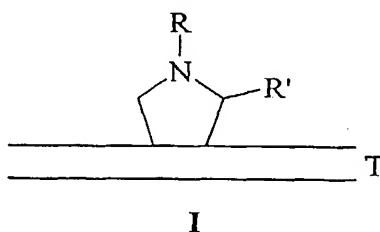
- adding, to a carbon nanotube, the compounds $R'-CHO$ and $R-NH-CHR''-COOR'''$ by a 1,3-dipolar cycloaddition, wherein:

- R and R' are as defined above;
- R'' is $-H$ or an amino acid side-chain;
- R''' is $-H$, an alkyl group of 1 to 5 carbon atoms, a $(CH_2CH_2O)_t-CH_3$ group, wherein t is an integer from 1 to 20, or an aromatic group;

to obtain a functionalized carbon nanotube of formula I, if appropriate protected;

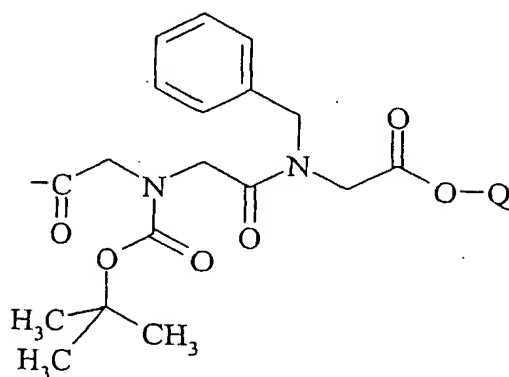
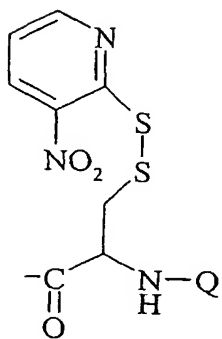
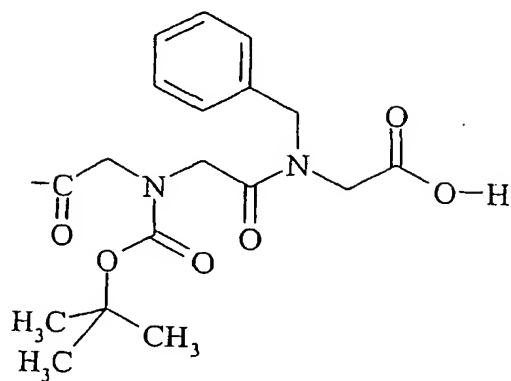
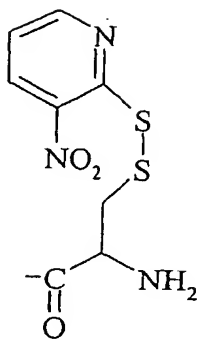
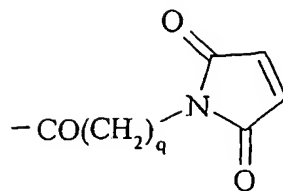
- if necessary, deprotecting the functionalized carbon nanotube of formula I, to obtain an unprotected functionalized carbon nanotube of formula I.

12. A process for preparing a functionalized carbon nanotube of the following formula I:



wherein T represents a carbon nanotube and independently from each other R and R' represent $-H$ or a group of formula $-M-Y-Z$, provided R and R' cannot simultaneously represent $-H$, wherein:

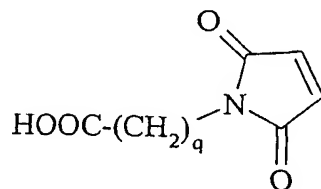
- $-M-$ is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising $-(CH_2)_r-$ or $-(CH_2-CH_2-O)_r-CH_2-CH_2-$, wherein r is an integer from 1 to 20;
- $-Y-$ is a group derived from a reactive group, such as a group selected from the list comprising, $-O-$, $-NH-$, $-COO-$, $-S-$, $-CH=$, $-CH_2-$, $-CC_kH_{2k+1}=$, wherein k is an integer from 1 to 10, in particular $-CCH_3=$, or $-CHC_kH_{2k+1}-$, wherein k is an integer from 1 to 10, in particular $-CHCH_3-$;
- $-Z$ is a linker group, liable to be linked to a P group, and if need be to release said P group, if appropriate protected by a capping or a protecting group $-Q$, such as a group of one of the following formulae:

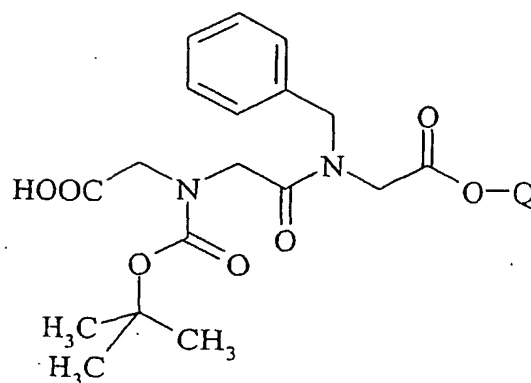
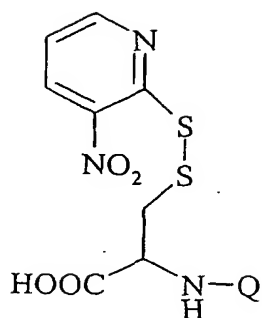


wherein q is an integer from 1 to 10;

said process comprising the following steps:

- adding to a unprotected functionalized carbon nanotube of formula I according to claim 11 a linker group of formula Z, if appropriate protected by a capping or a protecting group $-Q$, such as a group of one of the following formulae:



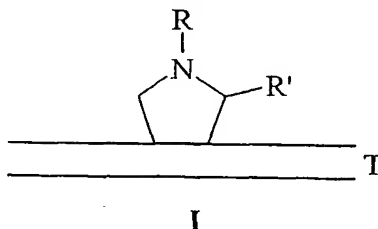


wherein q is an integer from 1 to 10;

to obtain a functionalized carbon nanotube of formula I, if appropriate protected;

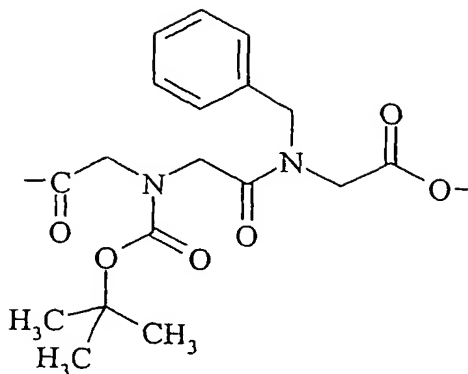
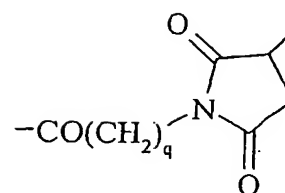
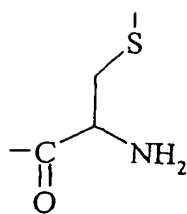
- if necessary, deprotecting the functionalized carbon nanotube of formula I, to obtain an unprotected functionalized carbon nanotube of formula I.

13. A process for preparing a functionalized nanotube of the following formula I:



wherein T represents a carbon nanotube and independently from each other R and R' represent -H or a group of formula -M-Y-Z-P or of formula -M-Y-P, provided R and R' cannot simultaneously represent -H, wherein:

- -M- is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising $-(CH_2)_r-$ or $-(CH_2-CH_2-O)_r-CH_2-CH_2-$, wherein r is an integer from 1 to 20;
- -Y- is a group derived from a reactive group, such as a group selected from the list comprising, -O-, -NH-, -COO-, -S-, -CH=, -CH₂-, -CC_kH_{2k+1}=, wherein k is an integer from 1 to 10, in particular -CCH₃=, or -CHC_kH_{2k+1}-, wherein k is an integer from 1 to 10, in particular -CHCH₃-;
- -Z- is a linker group, liable to be linked to a P group, and if need be to release said P group, such as a group of one of the following formulae:



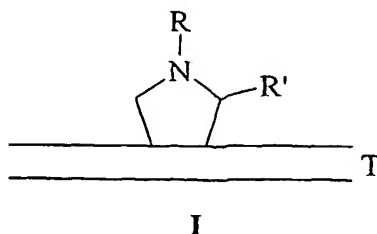
wherein q is an integer from 1 to 10;

- -P is an effective group allowing spectroscopic detection of said functionalized carbon nanotube, such as a fluorophore, such as FITC, or an active molecule, liable to induce a biological effect, if appropriate protected, such as an amino acid, a peptide, a pseudopeptide, a protein, such as an enzyme or an antibody, a nucleic acid, a carbohydrate, or a drug;

said process comprising the following steps:

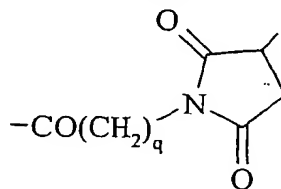
- adding to an unprotected functionalized carbon nanotube of formula I according to claim 11 or 12, an effective group or an active molecule of formula P, if appropriate protected, such as a fluorophore, such as FITC, an amino acid, a peptide, a pseudopeptide, a protein, such as an enzyme or an antibody, a nucleic acid, a carbohydrate, or a drug,
- or adding to an unprotected functionalized carbon nanotube of formula I according to claim 11, a group of formula Z-P, if appropriate protected, to obtain a functionalized carbon nanotube of formula I, if appropriate protected;
- if necessary, deprotecting the functionalized carbon nanotube of formula I, to obtain an unprotected functionalized carbon nanotube of formula I.

14. A process for preparing a peptide or protein functionalized carbon nanotube, of the following formula I:



wherein T represents a carbon nanotube and independently from each other R and R' represent H or a group of formula -M-Y-P, or of formula -M-Y-Z, provided R and R' cannot simultaneously represent -H, wherein:

- -M- is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising $-(CH_2)_r-$ or $-(CH_2-CH_2-O)_r-CH_2-CH_2-$, wherein r is an integer from 1 to 20;
- -Y- is a group derived from a reactive group, such as a group selected from the list comprising, -O-, -NH-, -COO-, -S-, -CH=, -CH₂-, -CC_kH_{2k+1}=, wherein n is an integer from 1 to 10, in particular -CCH₃=, or -CHC_kH_{2k+1}-, wherein k is an integer from 1 to 10, in particular -CHCH₃-;
- -Z- is a linker group, in particular a group of the following formula:



wherein q is an integer from 1 to 10;

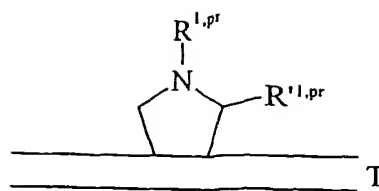
- -P is a peptide, in particular of following formula: $-[OC-CH(A_i)-NH]_t-H$, wherein -A_i is an amino acid side-chain, i is an integer from 1 to t and t is an integer from 1 to 150, advantageously from 1 to 50;

said process comprising the following steps:

- adding to a functionalized carbon nanotube of formula I, according to claim 11, a protected amino acid of the following formula:



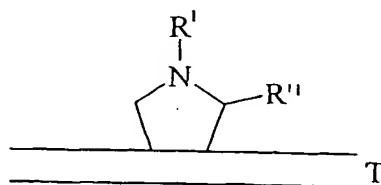
wherein -A_i is as defined above and -Q is a protecting group to obtain a functionalized carbon nanotube of the following formula II:



II

wherein independently from each other $R^{1,pr}$ and $R'^{1,pr}$ represent -H or a group of formula $-M-Y-OC-CH(A_i)-NH-Q$, or of formula $-M-Y-Z-OC-CH(A_i)-NH-Q$, wherein -M-, -Y-, -Z-, $-A_i$ and -Q are as defined above;

- deprotecting the functionalized carbon nanotube of formula II to obtain a functionalized carbon nanotube of the following formula III:



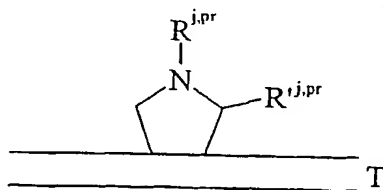
III

wherein independently from each other R^I and R^{II} represent -H or a group of formula $-M-Y-OC-CH(A_i)-NH_2$, or of formula $-M-Y-Z-OC-CH(A_i)-NH_2$, wherein -M-, -Y-, -Z-, and $-A_i$ are as defined above;

- adding to the functionalized carbon nanotube obtained at the preceding step a protected amino acid of the following formula:



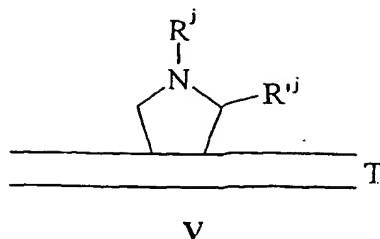
wherein $-A_i$ is as defined above and -Q is a protecting group to obtain a functionalized carbon nanotube of the following formula IV:



IV

wherein independently from each other $R^{j,pr}$ and $R'^{j,pr}$ represent -H or a group of formula $-M-Y-[OC-CH(A_i)-NH]_j-Q$, or of formula $-M-Y-Z-[OC-CH(A_i)-NH]_j-Q$, wherein -M-, -Y-, -Z-, $-A_i$ and -Q are as defined above, and j is an integer from 2 to t;

- deprotecting the functionalized carbon nanotube of formula IV to obtain a functionalized carbon nanotube of the following formula V:

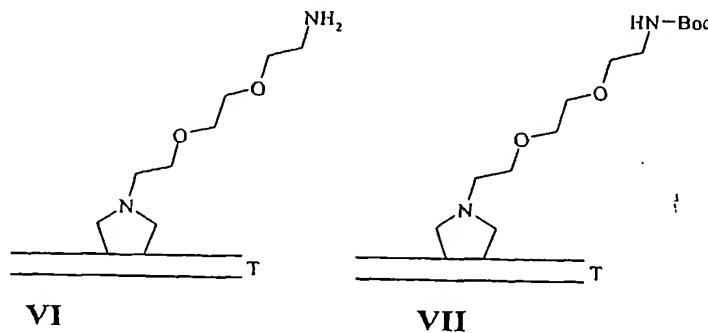


wherein independently from each other R^j and R^{ij} represent -H or a group of formula $-M-Y-[OC-CH(A_i)-NH]_j-H$, or of formula $M-Y-Z-[OC-CH(A_i)-NH]_j-H$, wherein -M-, -Y-, -Z-, and -A_i are as defined above, and j is an integer from 2 to t;

- repeating the last two steps t-1 times to obtain a peptide or protein functionalized carbon nanotube of formula I.

15. A process according to any of claims 12 to 14, wherein -Q is a capping group, such as CH_3CO- (acetyl), methyl, or ethyl, or a protecting group, such as a group selected from the list comprising methyl, ethyl, benzyl, *tert*-butyl, trityl, 3-nitro-2-pyridylsulfenyl, *tert*-butyloxycarbonyl (Boc), fluorenylmethyloxycarbonyl (Fmoc), benzylcarbonyl, trimethylsilylethylloxycarbonyl, phthalimide, or ethyleneoxy.

16. A process for preparing a functionalized carbon nanotube of one of the following formulae VI and VII:

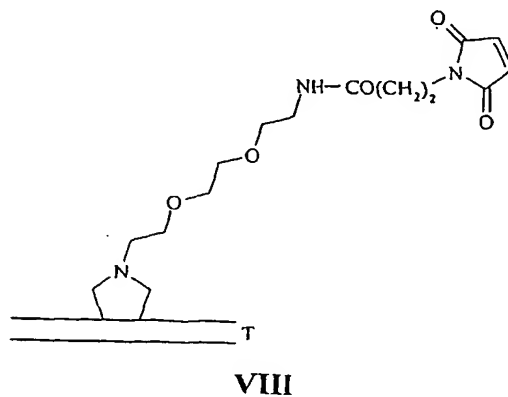


wherein T represents a carbon nanotube and Boc represents *tert*-butyloxycarbonyl, said process comprising the following steps:

- adding, to a carbon nanotube, the compounds $(CH_2O)_n$ (*para*formaldehyde) and $Boc-NH-(CH_2-CH_2-O)_2-CH_2-CH_2-NH-CH_2-COOH$ by a 1,3-dipolar cycloaddition, to obtain a protected functionalized carbon nanotube of formula VII;

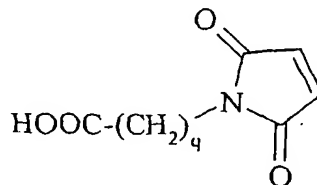
- if necessary, deprotecting the protected functionalized carbon nanotube of formula VII, to obtain an unprotected functionalized carbon nanotube of formula VI.

17. A process for preparing a functionalized carbon nanotube of the following formula VIII:



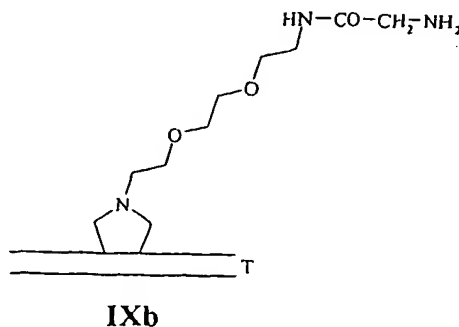
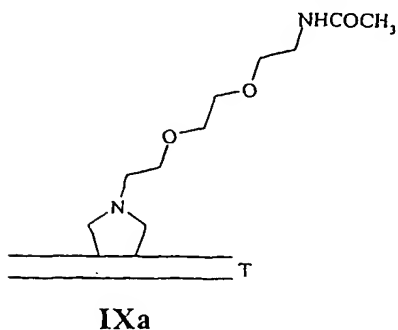
wherein T represents a carbon nanotube, said process comprising the following step:

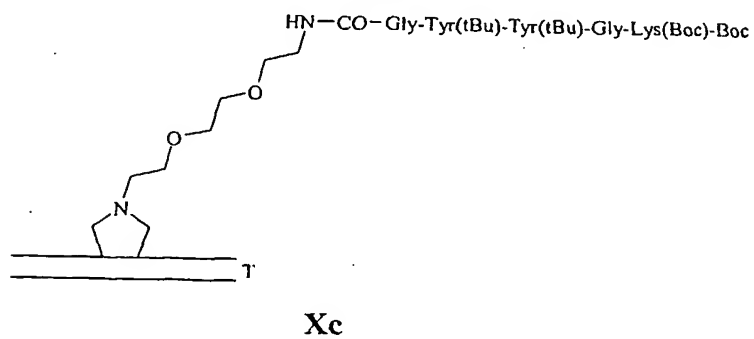
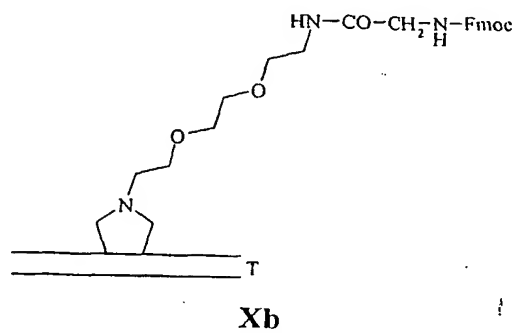
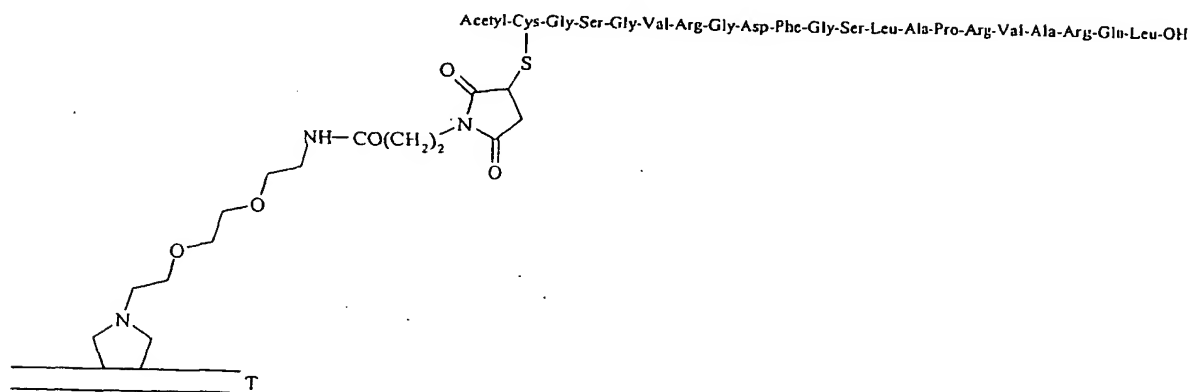
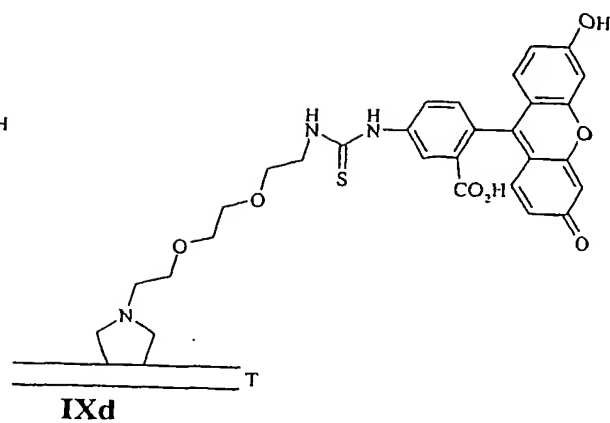
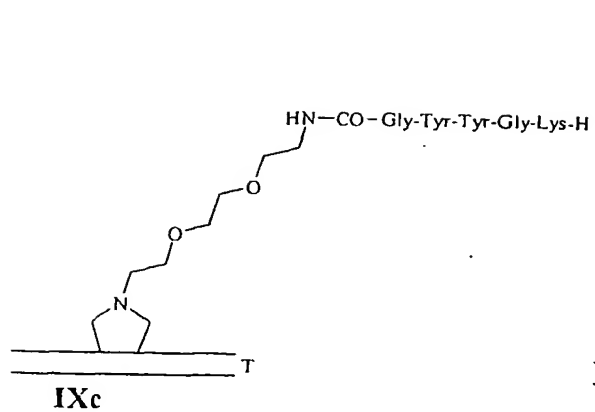
- adding, to a carbon nanotube of formula VI according to claim 16, a compound of the following formula:



to obtain a functionalized carbon nanotube of formula VIII.

18. A process for preparing a functionalized carbon nanotube of one of the following formulae IXa, IXb, IXc, IXd, IXe, Xb and Xc:





wherein T represents a carbon nanotube, Fmoc represents fluorenylmethyloxycarbonyl, tBu represents tert-butyl and Boc represents tert-butyloxycarbonyl, said process comprising the following steps:

- adding,
 - either to a functionalized carbon nanotube of formula VI according to claim 16, a group chosen among: $\text{CH}_3\text{-COOH}$, Fmoc-Gly-OH, Boc-Lys(Boc)-Gly-Tyr(tBu)-Tyr(tBu)-Gly-OH, or FITC,
 - or to a functionalized carbon nanotube of formula VIII according to claim 17, the following group, Acetyl-Cys-Gly-Ser-Gly-Val-Arg-Gly-Asp-Phe-Gly-Ser-Leu-Ala-Pro-Arg-Val-Ala-Arg-Gln-Leu-OH,to obtain a functionalized carbon nanotube of respective formula IXa, Xb, Xc, IXd or IXe;
- if necessary, deprotecting the functionalized carbon nanotube of formula Xb or Xc to obtain respectively the functionalized carbon nanotube of formula IXb or IXc.

19. A functionalized carbon nanotube such as obtained by the process of any of claims 11 to 18.

20. A pharmaceutical composition comprising as active substance at least one functionalized carbon nanotube according to any of claims 1 to 10 or 19, in association with a pharmaceutically acceptable vehicle, such as a liposome, a cyclodextrin, a microparticle, a nanoparticle, or a cell penetrating peptide.

21. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, as a pharmaceutical vehicle.

22. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the delivery of drugs, in particular for the intracellular delivery of drugs.

23. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the preparation of an immunogenic composition intended to provide an immunological protection to the individual to whom it has been administrated.

24. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the preparation of a medicament intended for the treatment or the prophylaxis of cancer, autoimmune or infectious diseases.

5 25. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the preparation of functionalized surfaces such as plastic or glass surfaces.

26. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the preparation of electrochemical biosensors.